



Supercapacitors for Extreme Environment Operations

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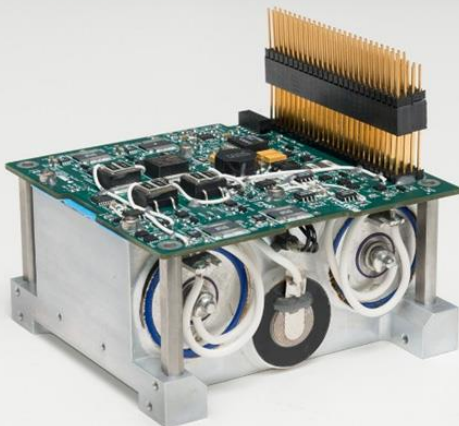
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Design Considerations

- **Double-layer capacitors are well suited for wide temperature operation**
 - Non-Faradaic charge storage eliminates kinetic limitations associated with electrode diffusion processes
 - Solid electrolyte interface (SEI) stability not a concern at elevated temperatures
 - Typically operate in the -40 to $+70^{\circ}\text{C}$ range
 - Limited largely by electrolyte *solvent properties*
- **Low temperature operation**
 - Acetonitrile electrolyte freezes between -40 and -50°C
 - Decreasing solvent conductivity and increasing cell resistance at low temperature
- **High temperature operation**
 - Acetonitrile electrolyte boils at 82°C
 - Reduced voltage window and electrolyte decomposition at elevated temperatures



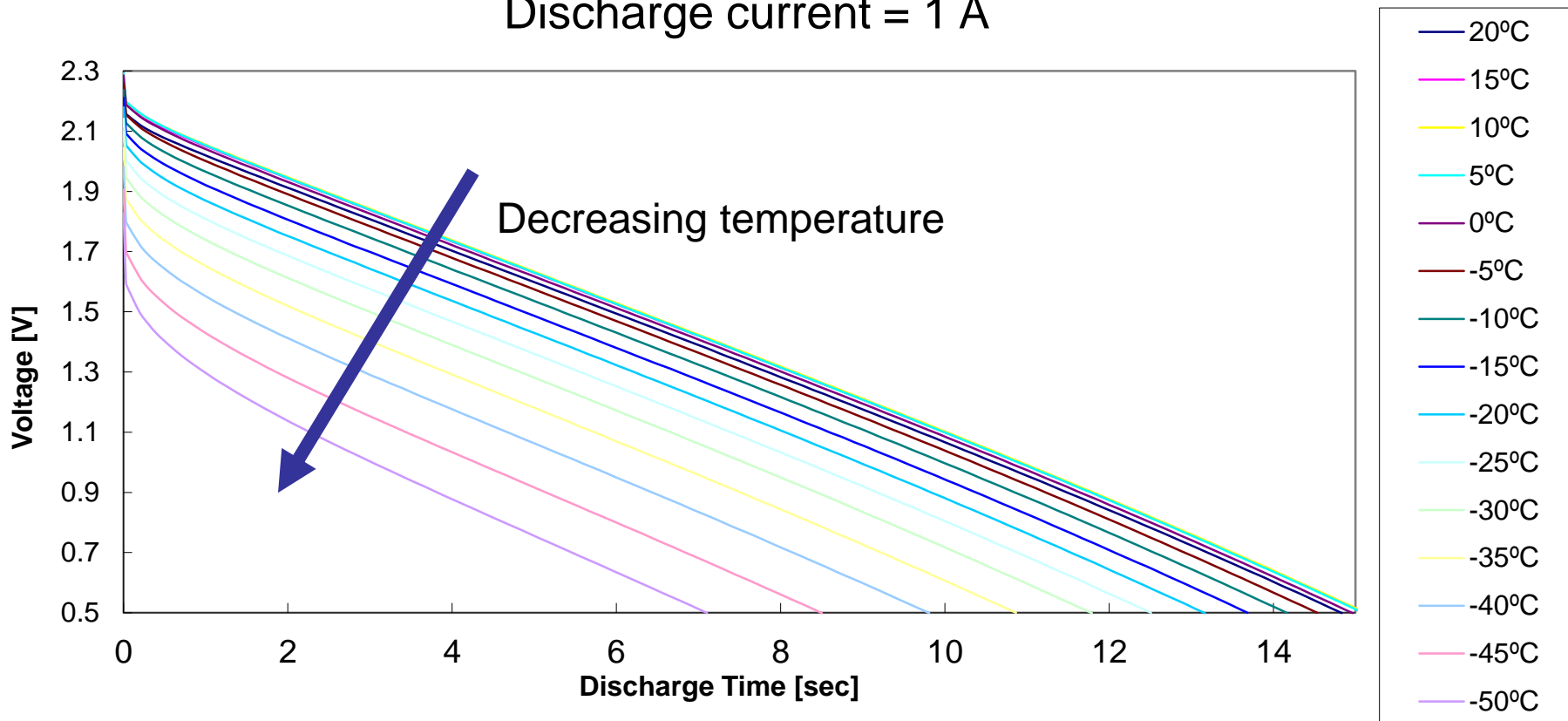
CSUNSat1 Hybrid Battery
"FM1-2"
2.5 Ahr Nameplate



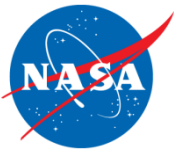


Representative Double-Layer Capacitor Response between +20°C and -50°C

10 F Maxwell Boostcap cell
Discharge current = 1 A

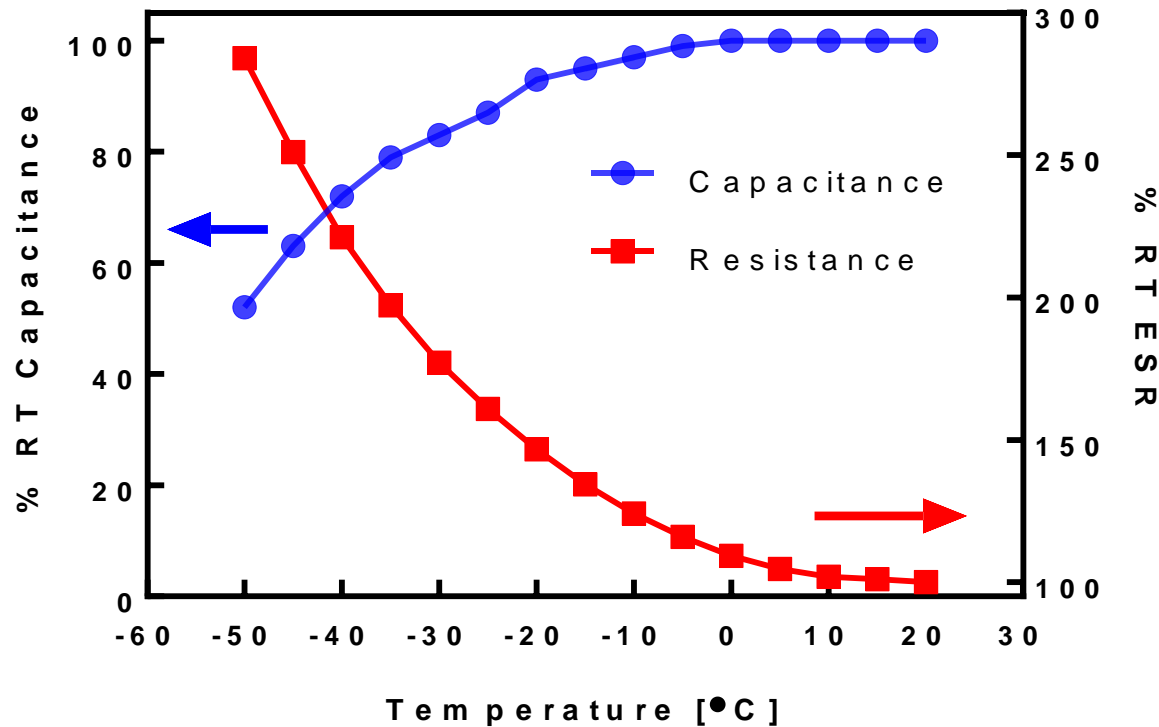


At temperatures $< -20^{\circ}\text{C}$, significantly increasing voltage drop
across internal resistance



Cell ESR More Sensitive to Temperature Than Capacitance

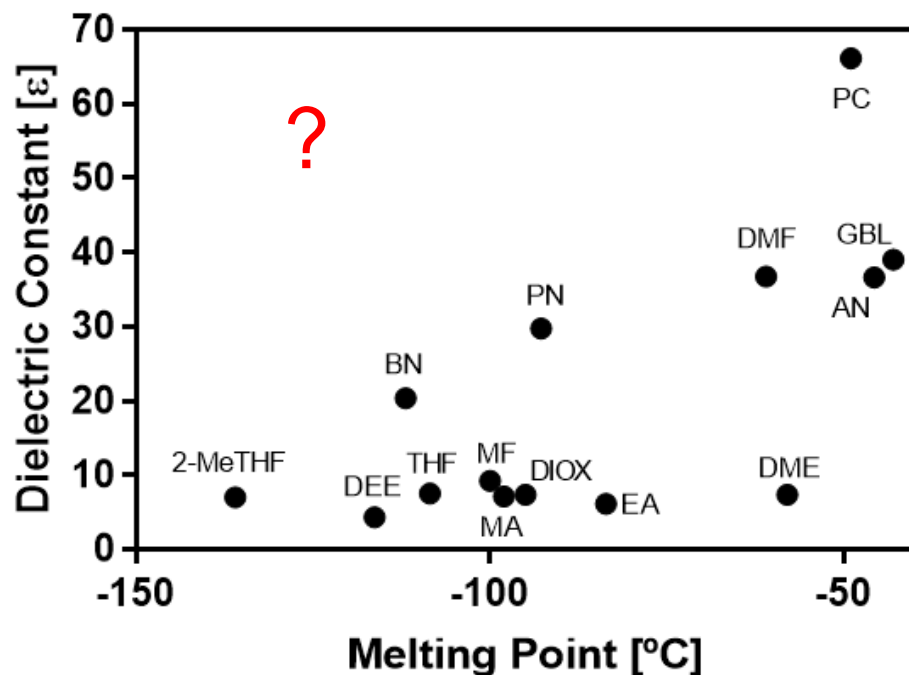
10 F Maxwell Boostcap cell
Discharge current = 1 A



- Increase in equivalent series resistance (ESR) more significant
- Capacitance response less sensitive
- Requires managing ESR increase



Solvent Blending Strategy



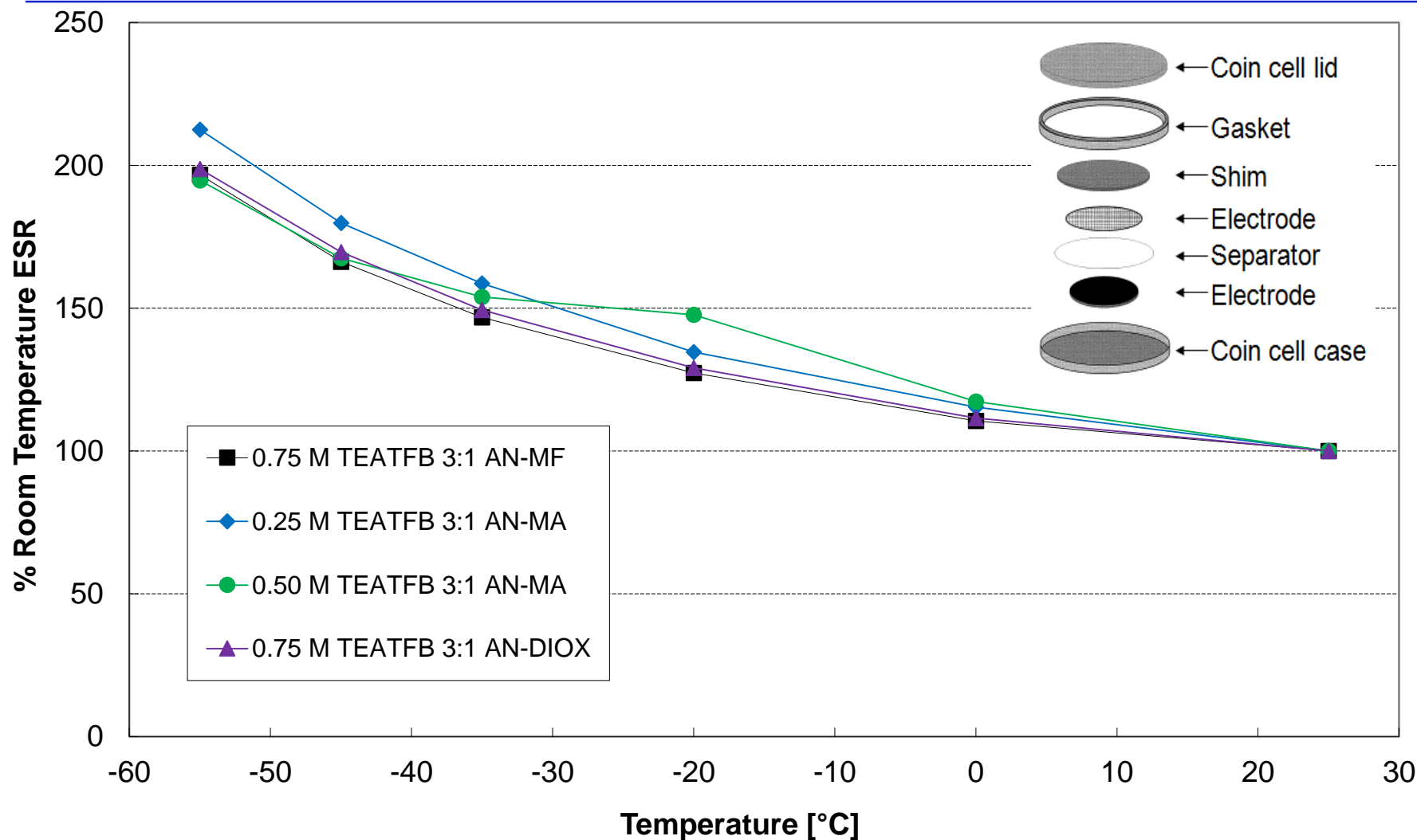
AN = acetonitrile
BN = butyronitrile
DEE = diethyl ether
DME = dimethyl ether
DMF = N,N-dimethyl formamide
DIOX = 1,3-dioxolane
EA = ethyl acetate
GBL = γ -butyrolactone
MA = methyl acetate
MF = methyl formate
PN = propionitrile
PC = propylene carbonate
THF = tetrahydrofuran
2-MeTHF = 2-methyl tetrahydrofuran

- Depress freezing point
- Maintain sufficient dielectric constant for high salt solubility

1. E.J. Brandon, W.C. West, M.C. Smart, L.D. Whitcanack, G. A. Plett, *J. Power Sources*, 170, 225 (2007).
2. W.C. West, M.C. Smart, E.J. Brandon, L.D. Whitcanack, G. A. Plett, *J. Electrochem. Soc.*, 155, A716 (2008).
3. Y. Korneblitt, A. Kajdos, W.C. West, M.C. Smart, E.J. Brandon, A. Kvit, J. Jagiello, G. Yushin, *Adv. Ener. Mater.* 22, 1655 (2012).



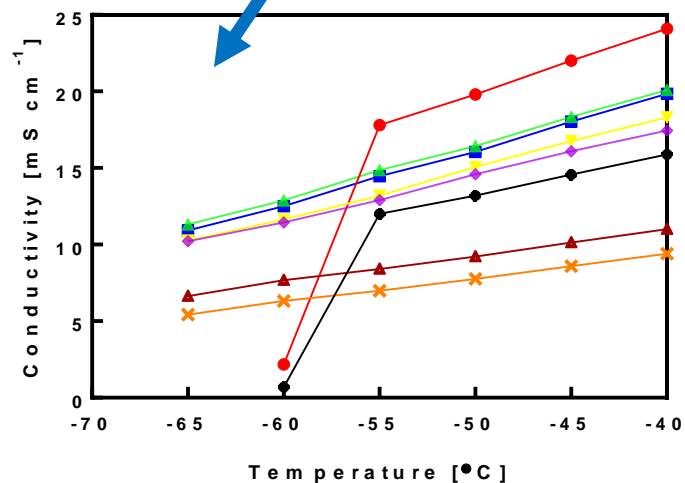
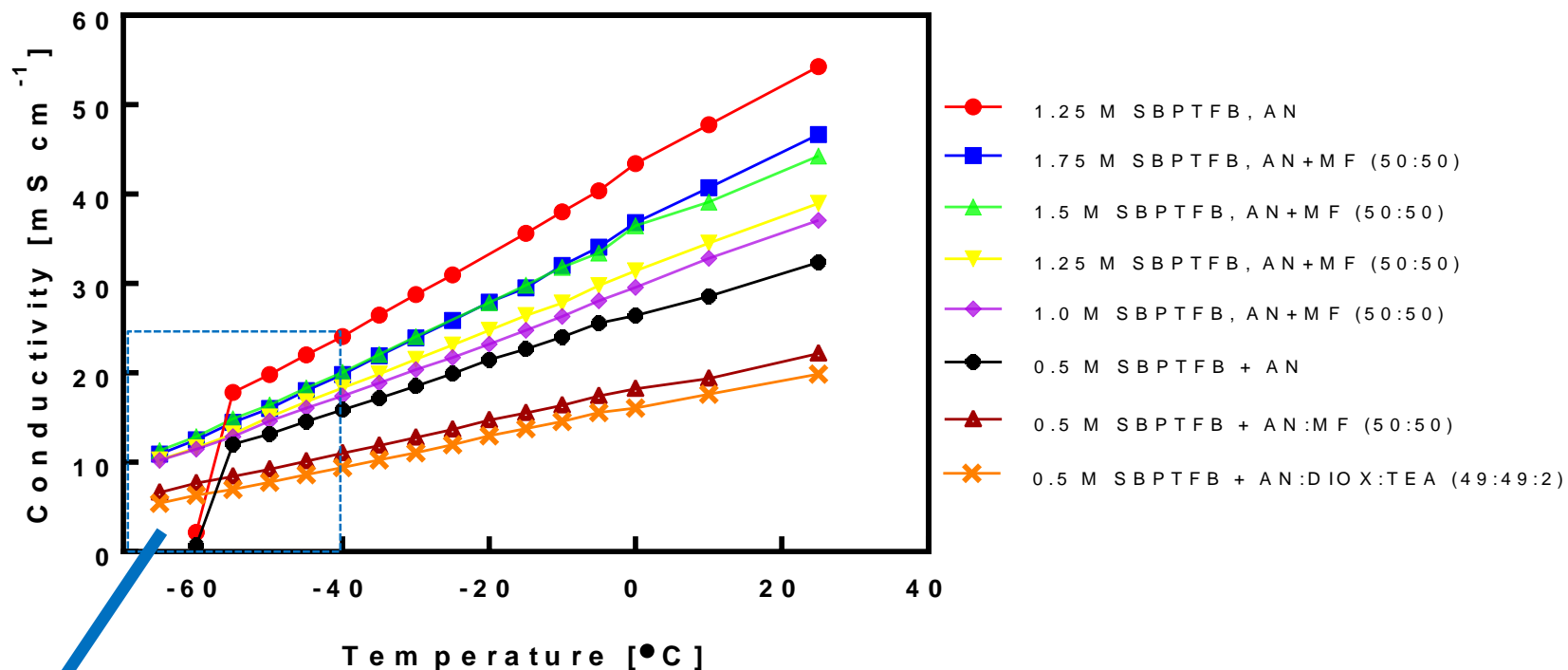
3:1 Solvent Blends Maintain Low ESR at Low Temperature



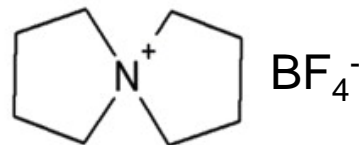
2032 format coin cell
Nuchar high surface area carbon electrode + Tonen PE separator



Conductivity of Low Temperature Blends

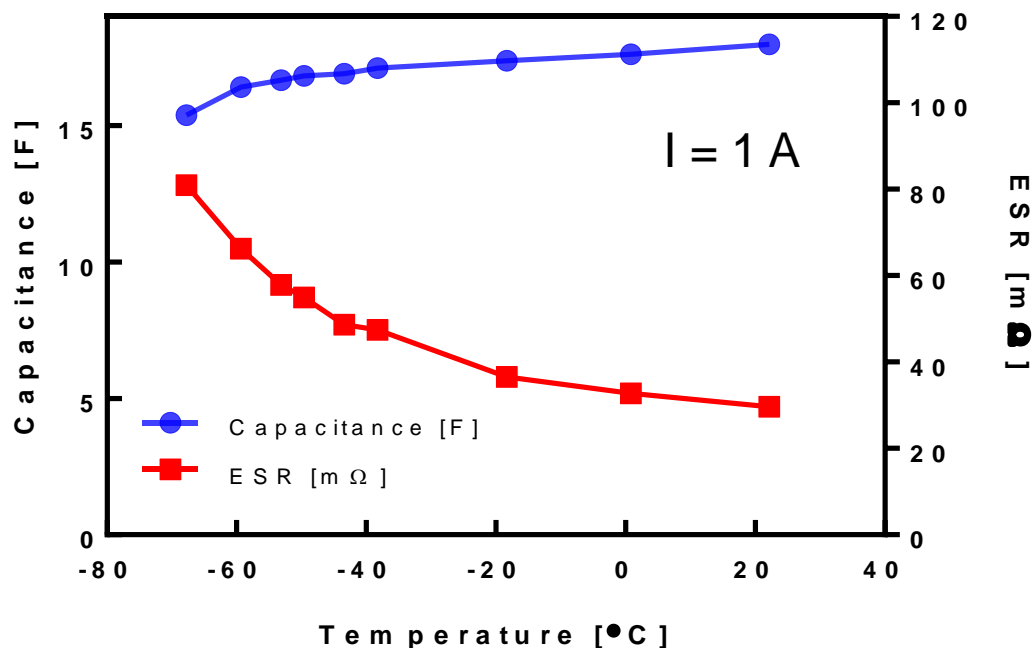


Used spiro-(1,1')-bipyrolidinium tetrafluoroborate (SBPTFB) in place of TEATFB salts





Operation of Cylindrical Cells to -70°C



Operation to -70°C through use of AN:MF modified electrolytes and standard high surface area carbon (YP-50)

Cells assembled at the Case Western University
Electrochemical Capacitor Prototyping Facility
(Robert Savinall and John Miller)

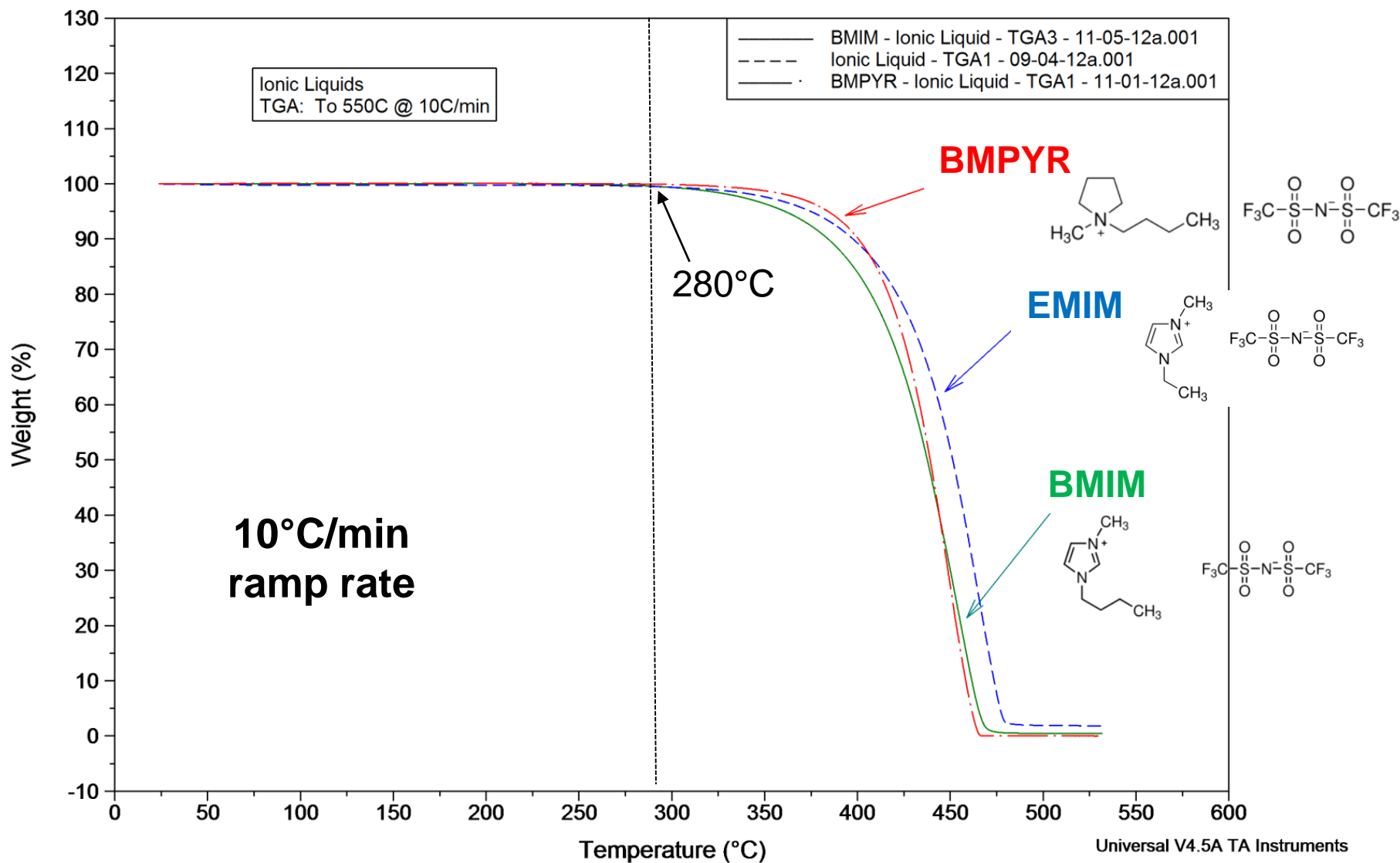


High Temperature Operation Electrode Options

- **Binder-free high surface area carbons**
 - Eliminate concerns over decomposition of binder
 - Difficult to scale-up with conventional current collectors
- **High surface area carbons with conventional binders**
 - More straightforward scale-up
 - More susceptible to thermally induced decomposition
 - May need to identify alternatives that are more stable



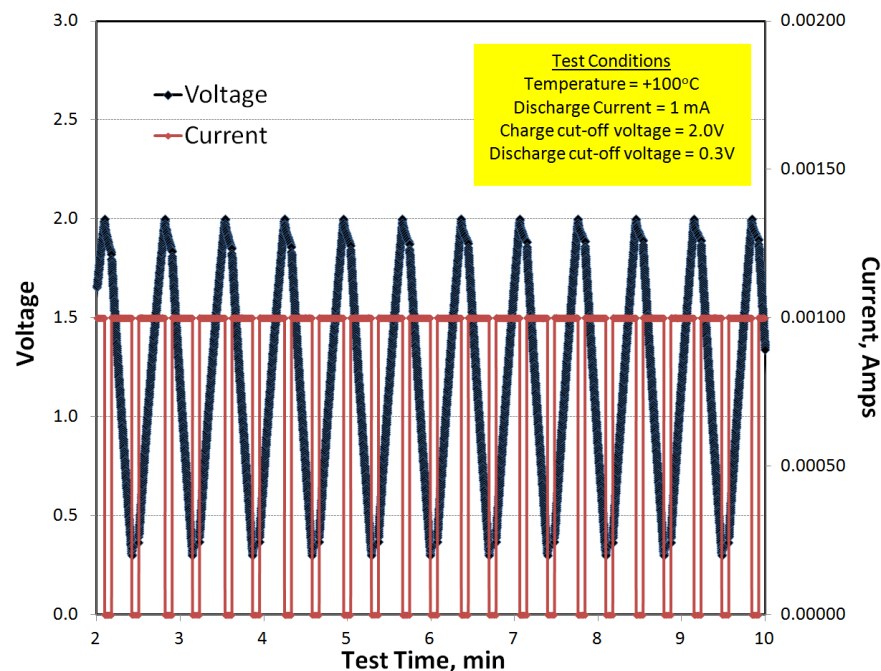
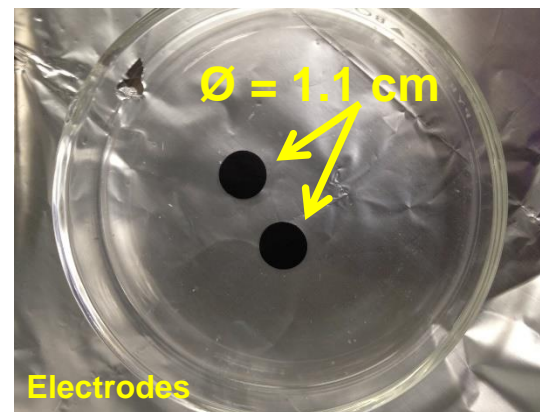
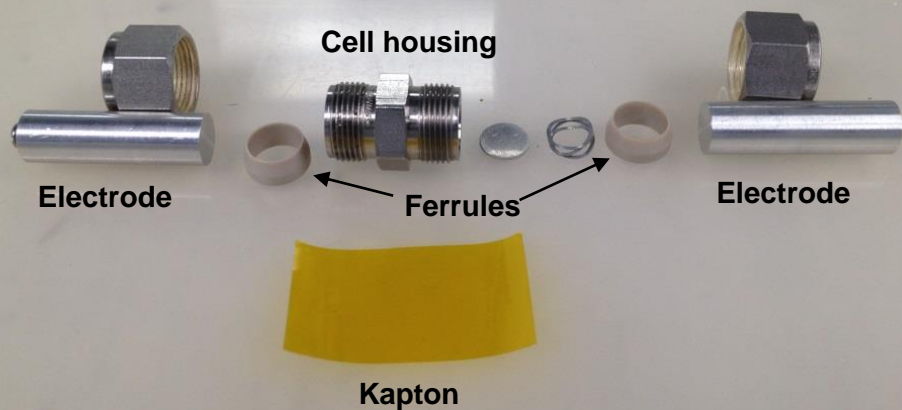
Ionic Liquid Thermogravimetric Analysis





Swagelok Cells for Longer Duration Cycling

Swagelok cells
(disassembled)

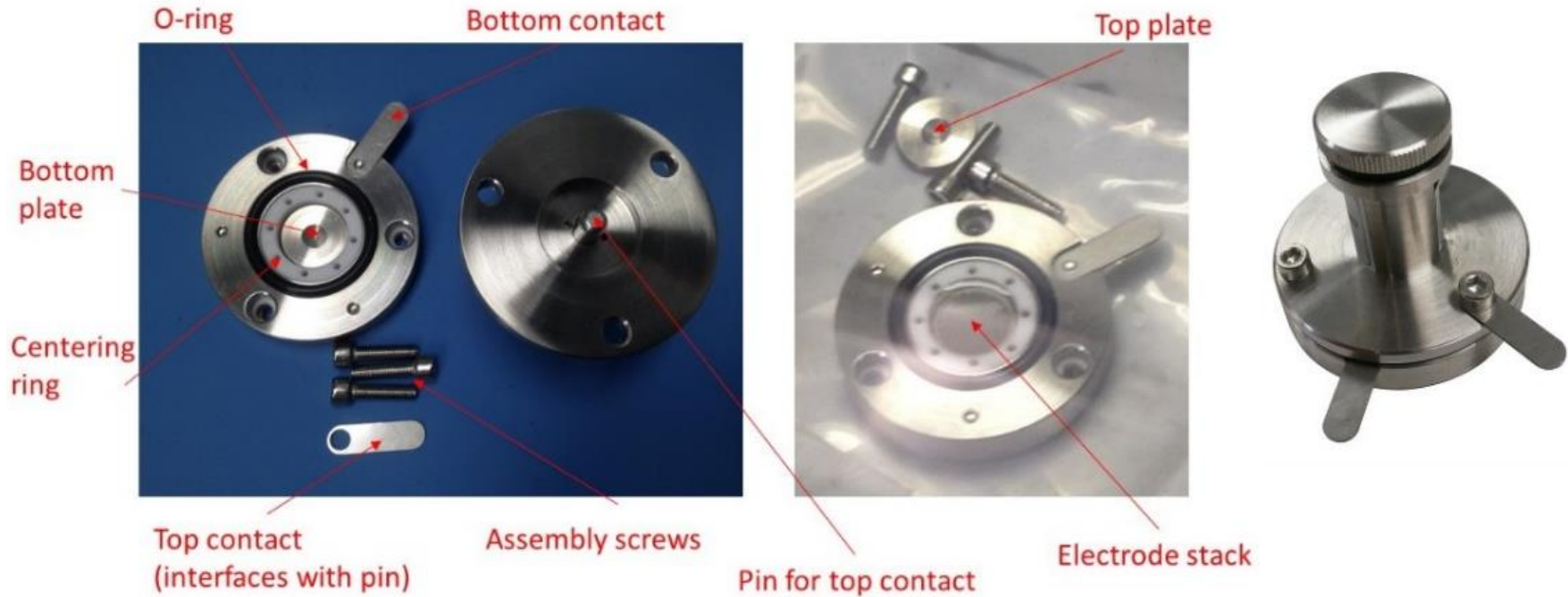


Swagelok
cells for high
temperature
prototype
testing

Swagelok cells
(sealed)



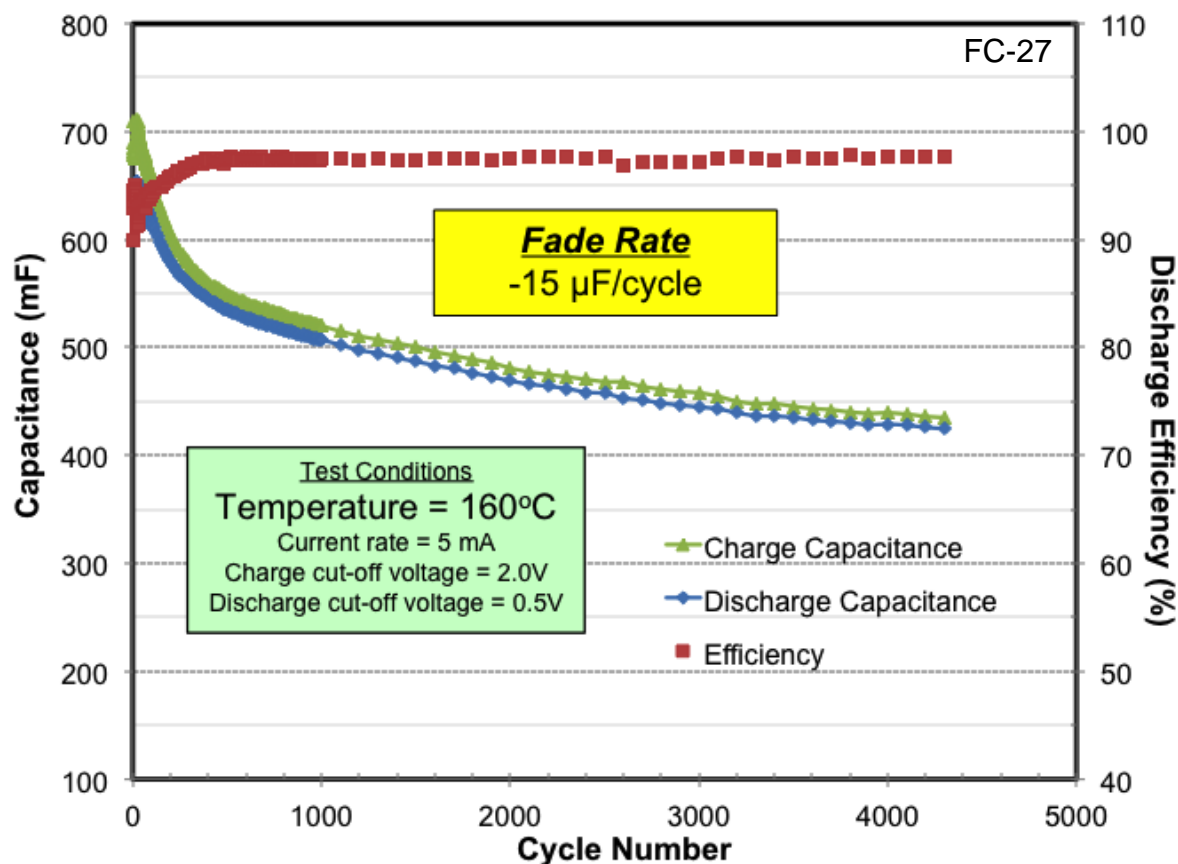
Flat Cell Housing with Coin Cell



Used in conjunction with coin cells, to maintain edge seal through static loading during high temperature testing



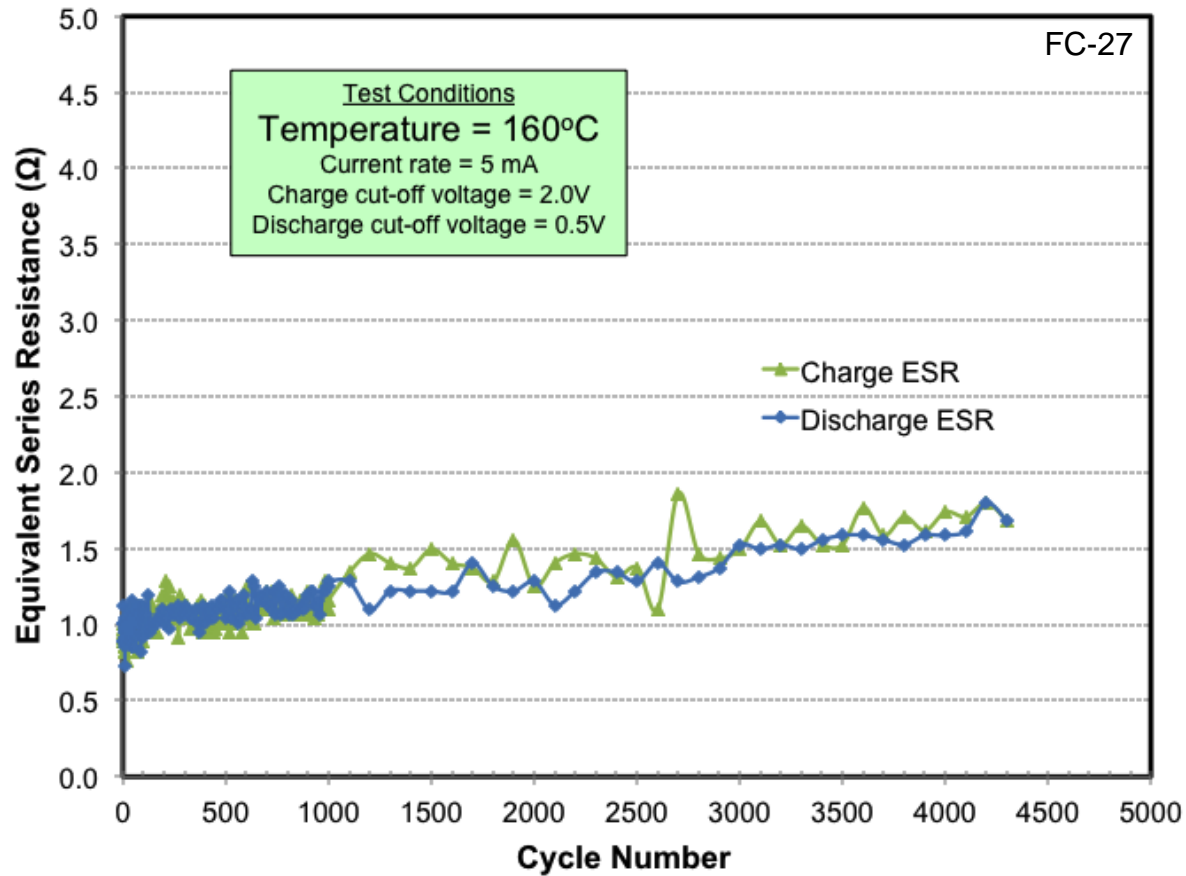
Initial Results with Spray Coated Electrodes



- Electrode: 90% Norit carbon, 5% acetylene black, 5% PTFE
- 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
- Polyimide-based separator (ceramic separators are difficult to implement)
- Voltage limits of 0.5V to 2.0V, based on application requirements
- Currently performing CV scans to better select voltage window



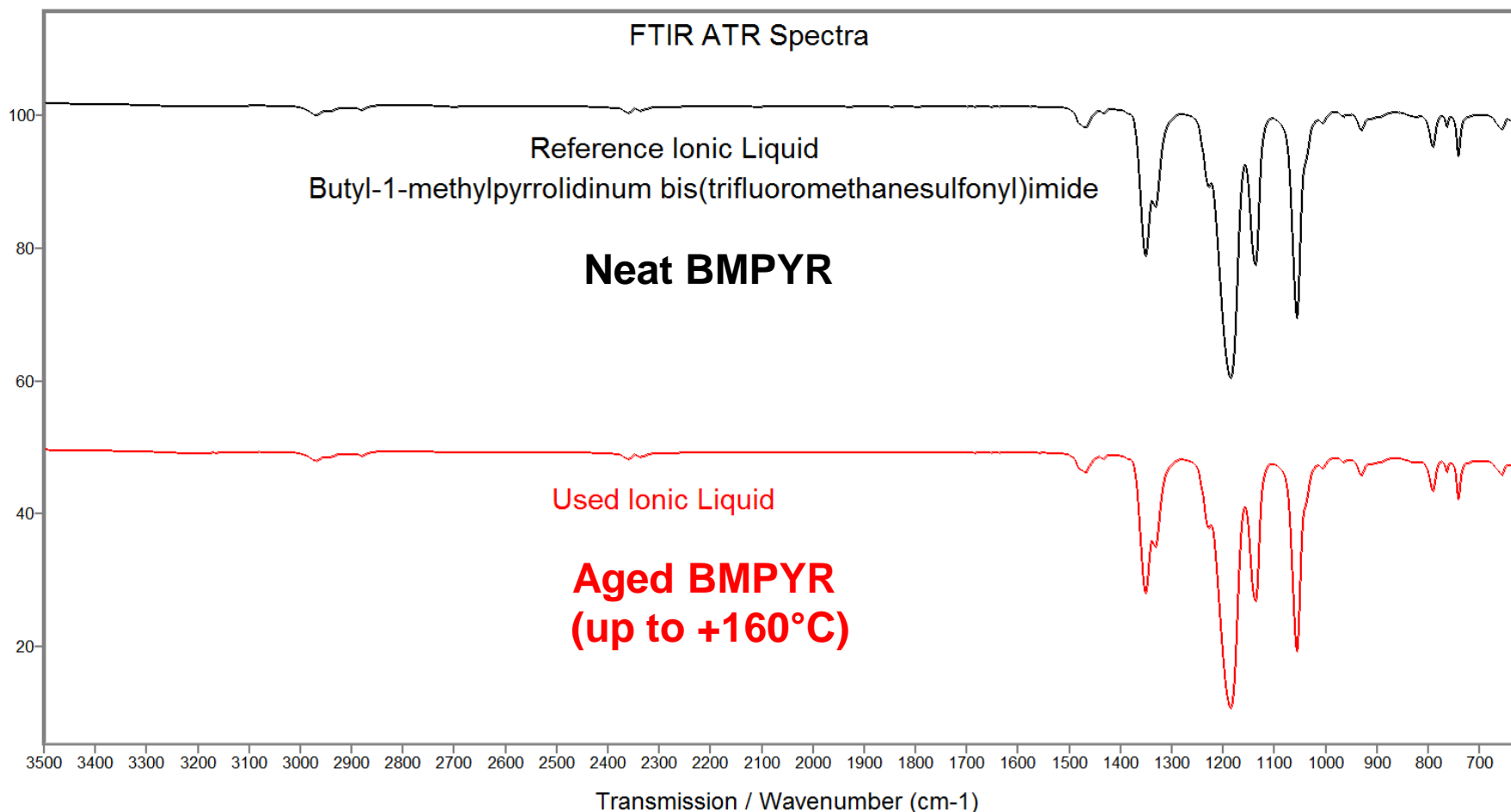
ESR Relatively Stable for Extended Cycling



Only moderate increases in ESR observed for >4000 cycles



Stability of Ionic Liquid



Extracted ionic liquid from 160°C treatment in Swagelok cell indicates no decomposition or reaction with cell components via FTIR spectroscopy (corroborated by NMR spectroscopy)



Summary

- Can extend operation to low temperatures through blending of organic solvents
- High temperature operation requires more extensive change in electrolyte (ionic liquids)
- Likely need to narrow the operating voltage window at 160°C
- Scale-up and testing of materials in larger format cells is ongoing





Acknowledgements

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